

**BABES BOLYAI UNIVERSITY  
FACULTY OF CHEMISTRY AND CHEMICAL ENGINEERING  
INORGANIC CHEMISTRY DEPARTMENT**

**COMPLEXES OF THE LACUNARY POLYOXOMETALATES  
WITH SPECIAL PROPERTIES AND APPLICATIONS**

*PhD Thesis  
ABSTRACT*

**Oana BĂBAN**

**Scientific advisor:  
Prof. Dr. Mariana RUSU**

**2011**

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**2011**

## Table of Contents

Introduction .....	2
I. General literature .....	6
I.1. Theoretical background .....	7
I.1.1. Heteropolyoxometalates with complete Keggin and Dawson structure and lacunary Keggin .....	7
I.1.2. Complexes of the monolacunary and trilacunary Keggin polyoxometalates	16
I.1.3. Applications of polyoxometalates .....	34
II. Original contributions .....	39
III. Synthesis .....	40
II.2. Characterization of a new polyoxotungstates complexes .....	43
II.2.1. Characterization of a new Keggin polyoxometalates of V(IV) with monolacunary ligands .....	43
II.2.1.1. Elemental chemical and thermogravimetric analysis.....	43
II.2.1.2. Vibrational spectroscopy FT-IR .....	44
II.2.1.3. Electronic spectroscopy .....	45
II.2.1.4. Electron spin resonance spectroscopy .....	52
II.2.1.5. Cyclic voltammetry .....	53
II.2.1.6. NMR Spectroscopy .....	58
II.2.1.7. X ray diffraction .....	59
II.2.2. Characterization of V(IV) complexes with an open Dawson-Wells structures .....	63
II.2.2.1. Elemental chemical and thermogravimetric analysis.....	64
II.2.2.2. Vibrational spectroscopy FT-IR .....	65
II.2.2.3. Electronic spectroscopy .....	68
II.2.2.4. Electron spin resonance spectroscopy .....	71
II.2.3. Characterization of new polyoxometalates with Ce (III) as a heteroatom ....	77
II.2.3.1. Elemental chemical and thermogravimetric analysis.....	79
II.2.3.2. Vibrational spectroscopy FT-IR .....	80
II.2.3.3. Electronic spectroscopy .....	82
II.2.4. Characterization of a new polyoxometalates with dinuclear metal clusters..	85
II.2.4.1. Characterization of a new polyoxometalates with dinuclear metal clusters:	

$K_{10}[M_2Bi_2W_{20}O_{70}] \cdot xH_2O$ (M=Mn(II), Co(II), Ni(II), Cu(II),) .....	87
II.2.4.1.1. Elemental chemical and thermogravimetric analysis.....	87
II.2.4.1.2. Vibrational spectroscopy FT-IR.....	88
II.2.4.1.3. Electronic spectroscopy .....	91
II.2.4.2.Characterization of a new polyoxometalates with dinuclear metal clusters:	
$K_{10}[(VO)_2Bi_2W_{20}O_{70}] \cdot 24H_2O$ and $K_{10}[(VO)_2Sb_2W_{20}O_{70}] \cdot 20H_2O$ .....	95
II.2.4.2.1. Elemental chemical and thermogravimetric analysis .....	98
II.2.4.2.2. Vibrational spectroscopy FT-IR.....	99
II.2.4.2.3. Electronic spectroscopy.....	102
II.2.4.2.4. Electron spin resonance spectroscopy .....	106
II.2.4.3. Characterization of a new polyoxometalates with dinuclear metal clusters:	
$Na_{10}[(UO_2)_2(H_2O)_2Bi_2W_{20}O_{70}] \cdot 34H_2O$ and	
$Na_{10}[(UO_2)_2(H_2O)_2Sb_2W_{20}O_{70}] \cdot 28H_2O$ .....	108
II.2.4.3.1. Elemental chemical and thermogravimetric analysis .....	108
II.2.4.3.2. Vibrational spectroscopy FT-IR.....	109
II.2.4.3.3. Electronic spectroscopy .....	116
II.2.5. Characterization of new polyoxometalates based on trilacunary fragments	122
II.2.5.1. Elemental chemical and thermogravimetric analysis .....	123
II.2.5.2. Vibrational spectroscopy FT-IR .....	128
II.2.5.3. Electronic spectroscopy .....	131
II.2.5.4. Magnetic susceptibility measurements .....	137
II.2.5.5. Electron spin resonance spectroscopy .....	139
II.2.5.6. Cyclic voltammetry .....	145
II.2.5.7. X ray diffraction .....	148
III. Experimental details .....	160
III.3.1. Synthesis of ligands polyoxometalates .....	161
III.3.2. Synthesis of complexes polyoxometalates .....	164
III.3.3. Instrumental Methods.....	172
IV. Special Applications of polyoxometalates .....	175
IV.4.1.Special Applications of polyoxometalates. Aerogels based on zirconium oxide doped with polyoxometalates .....	178

IV.4.1.1. Synthesis of gels and aerogels .....	182
IV.4.1.2. Raman spectroscopy of ZrO <sub>2</sub> aerogels doped with Yttrium .....	186
IV.4.1.3. X ray diffraction of ZrO <sub>2</sub> aerogels doped with yttrium .....	188
IV. 4.1.4. Specific surface area determened by BET method of ZrO <sub>2</sub> aerogels doped with polyoxometalates.....	197
IV.4.1.5. Raman and IR spectroscopy of ZrO <sub>2</sub> aerogels doped with polyoxometalates.....	199
IV.4.1.6. Determination of ionic conduction of ZrO <sub>2</sub> aerogels doped with polyoxometalates .....	205
IV.4.1.7. Cyclic voltammetry characterization of solid superacids based of ZrO <sub>2</sub> aerogels doped with polyoxometalates.....	209
IV.4.2. Special Applications of polyoxometalates Influence of polyoxometalates on the growth of barley .....	214
IV.4.3. Obtaining the necessary dilution and germination media.....	214
IV.4.4. Evolution of the growth of barley: results and discussion.....	216
Conclusions.....	232
Bibliography .....	238

Annex 1

Annex 2

Annex 3

Annex 4

Keywords

Polyoxometalates • Keggin • Dawson Wells • Vanadium • Spectroscopic  
measurements • Cyclic voltammetry • Dinuclear cluster • Sandwich-type  
complex •

## List of compounds described in this dissetation

1.  $K_5[PVW_{11}O_{40}] \cdot 14 H_2O$
2.  $K_5[AsVW_{11}O_{40}] \cdot 14 H_2O$
3.  $K_{11}[\{VO(H_2O)_3\}\{VO(K(H_2O)_2)\}(P_2W_{18}O_{66})] \cdot 28 H_2O$
4.  $K_{11}[\{VO(H_2O)_3\}\{VO(K(H_2O)_2)\}(As_2W_{18}O_{66})] \cdot 25 H_2O$
5.  $K_{19}[(BiW_9O_{33})_4\{WO_2(H_2O)\}_2Ce_3(H_2O)_8(Bi_4O_4)] \cdot 48 H_2O$
6.  $K_{15}[Ce_2(H_2O)_2(BiW_9O_{33})(W_5O_{18})_2] \cdot 21 H_2O$
7.  $K_{10}[Mn_2Bi_2W_{20}O_{70}] \cdot 24 H_2O$
8.  $K_{10}[Co_2Bi_2W_{20}O_{70}] \cdot 24 H_2O$
9.  $K_{10}[Ni_2Bi_2W_{20}O_{70}] \cdot 24 H_2O$
10.  $K_{10}[Cu_2Bi_2W_{20}O_{70}] \cdot 24 H_2O$
11.  $K_{10}[(VO)_2Bi_2W_{20}O_{70}] \cdot 24 H_2O$
12.  $K_{10}[(VO)_2Sb_2W_{20}O_{70}] \cdot 20 H_2O$
13.  $Na_{10}[(UO_2)_2(H_2O)_2Bi_2W_{20}O_{70}] \cdot 34 H_2O$
14.  $Na_{10}[(UO_2)_2(H_2O)_2Sb_2W_{20}O_{70}] \cdot 28 H_2O$
15.  $Na_{12}[Cu_3(H_2O)_3BiW_9O_{33}]_2 \cdot 26 H_2O$
16.  $Na_6H_4[\{Mn(H_2O)_3\}_2(WO_2)_2(BiW_9O_{33})_2] \cdot 41H_2O$
17.  $Na_6H_4[\{Co(H_2O)_3\}_2Co(H_2O)_2\}(WO_2)(BiW_9O_{33})_2] \cdot 27H_2O$

## Introduction

The work done as part of this thesis was principally oriented towards the synthesis and characterization of a new compounds belonging to the family of polyoxometalates. Resulting from the polycondensation of the metallic oxoanions with oxoanions of the same or different species, they have considerably developed and diversified in our days. Polyoxometalates are early transition metal oxygen anion clusters. More specifically, they are oligomeric aggregates of metal cations (usually the  $d^0$  species V(V), Nb(V), Ta(V), Mo(VI), and W(VI)) bridged by oxide anions that are formed by self-assembly processes. Two generic families of polyoxometalates exist. These are the isopoly compounds, (also called isopolyanions or isopolyoxometalates) which contain only the  $d^0$  metal cations and oxide anions and the heteropoly compounds (also called heteropolyanions or heteropolyoxometalates) which contain one or more p-, d-, or f-block "heteroatoms" in addition to the other ions.

Polyoxometalates, owing to their remarkable properties, are more involved in up- to- date domains, like: homogeneous and heterogeneous catalysis, obtaining of active substances with antiviral and antitumoral action, thin- layer chromatography, obtaining of ion- selective membranes or obtaining of corrosion inhibitors. Polyoxometalates arouse interest in the research of this field, which offers and opens up unpredictable prospects to the science of chemistry.

Although they have been investigated since the last third of the XIX-th century, it is only in the last 40-50 years that modern experimental techniques revealed a large variety in structures and in properties of these substances. However fundamental questions regarding the limits of the composition, size and structure, mechanism of synthesis and reactivity, still remain unanswered.

Polyoxometalates are metal-oxygen clusters that exhibit a fascinating variety of structures and properties, including size, shape, charge, density, acidity, redox states, stability, solubility, etc. Transition metal substituted polyoxometalates have attracted a continually growing interest in the field of polyoxometalate chemistry, being of great interest in catalysis, material science and medicine.

The great advantage of these complexes is the possibility to vary either the type of the metallic cluster, its structural topology and the nature of the transition

metals, or the heteroatom. The proximity of the transition metals possessing unpaired electrons favors their coupling through the exchange, superexchange or dipolar interactions. These are the starting points for the magnetic clusters formation. The metallic cluster is usually encapsulated between two Keggin or Dawson-Wells trivacant fragments.

The aim of this thesis entailed the investigation of the formation reaction as well as of the physico-chemical properties of a new complexes with lacunary polyoxometalate structure. The formation of polyoxometalates, and especially the rational directed synthesis of specific structures presents a major challenge.

*The present dissertation is divided in four parts:*

- *part I* contains a study of the chemistry of the Keggin and Dawson Wells type polyoxometalates, especially of the mono- and trilacunary type and their complexes and their most important applications.
- *part II* contains the original results obtained through the research period. The physico-chemical characterization of the lacunary polyoxometalates complexes are also discussed here. Methods used in the physico-chemical characterization lacunary polyoxometalates complexes include elemental and thermogravimetric analysis, vibrational (FT-IR, Raman), electronic (UV-VIS) and multinuclear NMR spectroscopy, magnetic susceptibility measurements as well as cyclic voltammetry.
- Partea a II-a conține rezultatele originale obținute în perioada de cercetare.
- *part III* is dedicated to experimental details of the preparation of newly obtained compounds.
- *part IV* relieve the catalytic properties of polyoxometalates complex and the influence of polyoxometalates on the on the growth of barley.



## Synopsis of the main part of the thesis

The chapter called “**Characterization of a new Keggin polyoxometalates of V(IV) with monolacunary ligands**” contains the detailed analyses of the two new  $K_5[PVW_{11}O_{40}] \cdot 14 H_2O$  ,  $K_5[AsVW_{11}O_{40}] \cdot 14 H_2O$  complexes. The V(IV) substituted Keggin polyoxotungstophosphate and polyoxotungstoarsenate in aqueous solution were synthesized, by the direct addition of vanadyl sulfate to a solution of the trilacunary  $\alpha$ -Keggin polyoxotungstate anion. The reaction mechanism involves V(IV) metal cations insertion and transformation of the trilacunary  $[\alpha-PW_9O_{34}]^{9-}$  ,  $[\alpha-AsW_9O_{34}]^{9-}$  to the monolacunary  $[\alpha-PW_{11}O_{39}]^{7-}$  ,  $[\alpha-AsW_{11}O_{39}]^{7-}$  fragment. The EPR spectra confirm that the unpaired electron delocalization is towards the oxygen atoms from V-O<sub>b,c</sub> bonds. Electronic and EPR spectra indicate  $O_h$  local symmetry for vanadium ion in  $K_5[PVW_{11}O_{40}] \cdot 14 H_2O$  ,  $K_5[AsVW_{11}O_{40}] \cdot 14 H_2O$  compounds. The IR spectra show that the  $\alpha$ -K<sub>7</sub>[PW<sub>11</sub>O<sub>39</sub>] and  $\alpha$ -K<sub>7</sub>[AsW<sub>11</sub>O<sub>39</sub>] act as pentadentate ligand with coordination involving the oxygen atoms of monolacunary cavity. Crystalline structure of the compound  $K_5[P(VO)W_{11}O_{39}] \cdot 14H_2O$  consists of discrete anions of  $\alpha$ -[P(VO)W<sub>11</sub>O<sub>39</sub>]<sup>5-</sup>, K<sup>+</sup> cations and water molecules, some of which were coordinated to the potassium cations. These complexes are bound by six oxygen atoms from corner-sharing octahedra and can obtain a supramolecular structure which could incorporate other cations even lanthanides, 11 *octahedra* WO<sub>6</sub> and octahedron VO<sub>5</sub>(H<sub>2</sub>O) are equivalent to a saturated Keggin structure, VO<sub>5</sub>(H<sub>2</sub>O) octahedron is delocalized over the 12 equivalent positions in a complete Keggin structure.

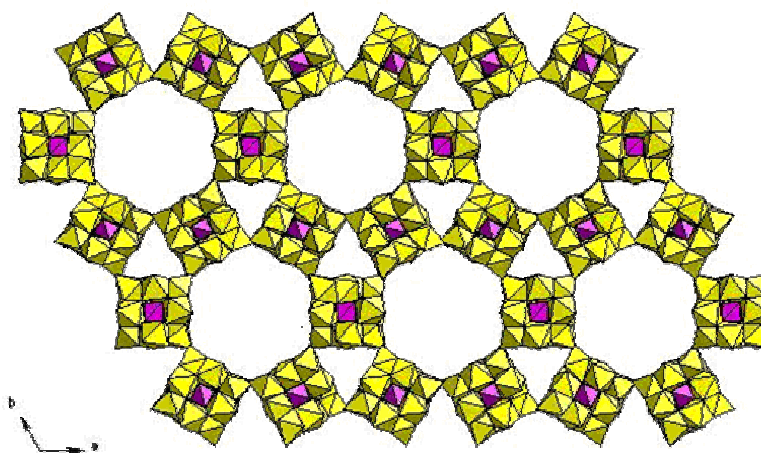


Figure 1. Supramolecular structure of the  $K_5[PV^{IV}W_{11}O_{40}] \cdot 14 H_2O$  complex.

The chapter called “**Characterization of V(IV) complex with an open Dawson-Wells structures**” contains details about two complexes



for who we propose in the first case a Wells-Dawson structure, but after the chemical analysis and spectrometrical measurements we observe that for those compounds correspond an open Wells-Dawson structure. The  $\alpha$ -[As<sub>2</sub>W<sub>18</sub>O<sub>66</sub>]<sup>14-</sup>,  $\alpha$ -[P<sub>2</sub>W<sub>18</sub>O<sub>66</sub>]<sup>14-</sup> anions are an intermediate species in the formation of the Wells–Dawson tungstoarsenate, tungstophosphate, not known at the present time. It has an open structure which is stabilized by inclusion of a potassium cation, and closing of the structure needs elimination of this cation. It constitutes a new type of inorganic ligand. Usually, ligand behaviour of polyoxometalates in solution results from the elimination of oxotungsten fragments of a complete structure. Here it is a consequence of the opening of the complete structure, which generates terminal oxygen atoms in such a manner that they define a coordination site very reactive towards alkali and transition metal cations. Topology and size of this site allow the fixation of several cations with different modes of coordination and offer the possibility to functionalize the transition metals by substitution of the water ligands.

The complexes have an open structure that is stabilized by the inclusion of potassium cation and two groups of vanadyl.

The chapter called “**Characterization of new polyoxometalates with Ce (III) as a heteroatom**” focuses on the different coordination geometries of the lanthanide cations and the vacant sites afforded by the polyoxometalates usually result in large oxometalate clusters, showing very interesting electroluminescence and photoluminescence activity. Trivalent Keggin fragments of  $[\alpha\text{-B-X}^{III}\text{W}_9\text{O}_{33}]^{9-}$  (X- Sb, Bi) type are suitable building for synthesis of large polyoxotungstates The species consist of two, three, four, six and twelve  $[\alpha\text{-B-X}^{III}\text{W}_9\text{O}_{33}]^{9-}$  units which are linked by lanthanide cations in order to form new classes of material with a large anion cluster. The obtained complexes are composed by cerium (III) cations,  $[\alpha\text{-B-BiW}_9\text{O}_{33}]^{9-}$  Keggin lacunary units and  $[W_5O_{18}]^{6-}$  or Bi<sub>4</sub>O<sub>4</sub> cluster. Every Ce (III) ion achieves a distorted square-antiprismatic eight-fold coordination by the oxygen atoms.

The chapter called “**Characterization of a new polyoxometalates with dinuclear metal clusters**” describes a series of sandwich-type complexes.

A special class of heteropolyoxometalates is the unsaturated trilacunary Keggin-type  $[X^{n+}W_9O_{33}]^{(12-n)-}$  structure, where the heteroatom X is one of the  $Sb^{III}$   $Bi^{III}$  ions. The main characteristic of these ions is the presence of one pair of electrons which prevents further condensation to a saturated Keggin structure. However, transition metal ions could link the lacunary units, resulting a sandwich-type structure.

In Figure 2 is depicted the polyhedral plot of this type of compounds. Two  $\beta$ - $B$ - $XW_9$  subunits (X- Sb, Bi) are linked together by two corner-sharing  $WO_6$  octahedra. Furthermore, two transition-metal atoms are bonded through two oxygen atoms of one unit and one oxygen atom of the other unit to the tungsten-oxygen framework. Formally, the *fac*- $WO_3$  groups have been exchanged for transition-metal ions with three aquo ligands.

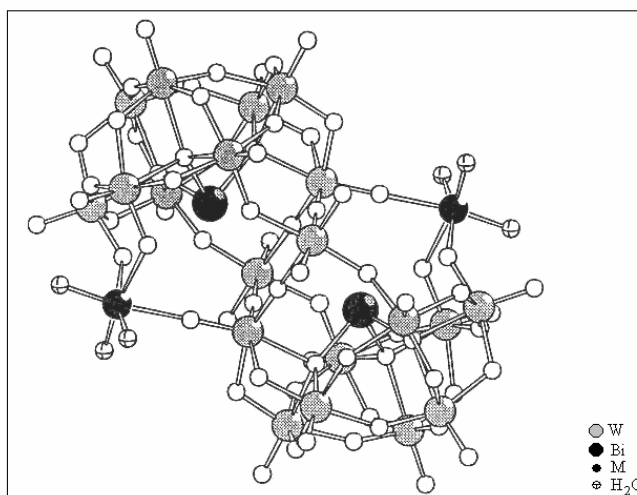


Figure 2. The structure of the  $[Bi_2M_2W_{20}M_2O_{70}(H_2O)_6]^{(14-2n)-}$  polyoxometalate.

This unusual formation leads to three free coordination sites at the transition-metal atoms that are completed by water molecules.  $[Mn^{+2}Bi_2W_{20}O_{70}(H_2O)_6]^{(14-2n)-}$ , polyoxometalates are usually synthesized from their complete  $B$ - $\beta$ - $[Bi_2W_{22}O_{74}(OH)_2]^{12-}$ , precursor structure by the removal of two  $WO_6$  octahedra and have substituted with transition metal cations. They exhibit an increased reactivity towards metal ions, thus forming a broad variety of complexes in which the polyoxoanion framework remains unchanged.

According to our studies, we recommend for the uranyl complexes polyoxometalates a “sandwich” kind of structure, which consist of two B-β-[XW<sub>9</sub>O<sub>33</sub>] fragments (X- Sb, Bi) united by two uranyl ions and two WO<sub>6</sub> fragments. Each uranium atom adopt the bipyramidal pentagonal coordination, forming two equatorial bonds to the terminal oxygens of a pair of two WO<sub>6</sub> octahedra bonded by common edges which belong to one of the B-β-[XW<sub>9</sub>O<sub>33</sub>] fragments (X- Sb, Bi) and a bond to the terminal oxygen of one of the WO<sub>6</sub> fragment, the other two equatorial coordinating points being satisfied by two molecules of water. Generally, in polyoxometalate complexes, the UO<sub>2</sub><sup>2+</sup> group is linear and normal to the equatorial plane formed by the oxygen atoms from the complex. Therefore, the polyoxometalate ligands form strong bonds with uranium by lowering the order of the U=O band and consistently lowering the ν<sub>as</sub>(O=U=O) frequency.

The chapter called **“Characterization of new polyoxometalates based on trilacunary fragments”**: present the way of obtaining in the same reaction condition of three types of polyoxometalats with different structures: [Cu<sub>3</sub><sup>2+</sup>(H<sub>2</sub>O)<sub>3</sub>(BiW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>]<sup>12-</sup> Hervè type, [Mn<sub>2</sub><sup>2+</sup>(H<sub>2</sub>O)<sub>6</sub>(BiW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>(WO<sub>2</sub>)<sub>2</sub>]<sup>10-</sup> and [Co<sub>3</sub><sup>2+</sup>(H<sub>2</sub>O)<sub>8</sub>(BiW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>(WO<sub>2</sub>)<sub>2</sub>]<sup>10-</sup> Krebs type and their crystal structure.

In the case of the sodium salt of [Cu<sub>3</sub>(BiW<sub>9</sub>O<sub>33</sub>)<sub>2</sub>(H<sub>2</sub>O)<sub>3</sub>]<sup>12-</sup>, who present a Hervè structure, polyoxoanion consists of to α-B-[BiW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> anions which linked by O-Cu-O bridges (Figure 3.). Each Cu shares an oxygen with each two W atoms in each α-B- [BiW<sub>9</sub>O<sub>33</sub>]<sup>9-</sup> unit and water molecule lies at the apex of a square-pyramidal coordination group. Three Na cations are closely associated with the anion, being coordinated in a local equatorial mirror plane between the Cu atoms. Each Na is linked to two Cu- bonded oxygens of each of two W atoms in each α-B-{BiW<sub>9</sub>O<sub>33</sub>}, and is also bonded to two H<sub>2</sub>O ligands which complete a distorted trigonal-prismatic NaO<sub>6</sub> group. In each half –anion, the W atoms linked through O to the same Cu share octahedral corners, and those linked to the same Na share octahedral edges.

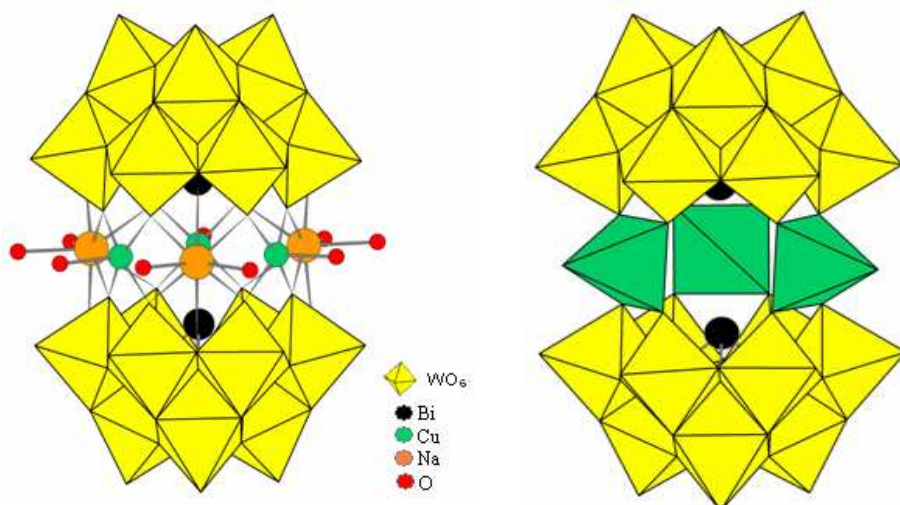


Figure 3. The structure of the  $\text{Na}_{12}[\text{Cu}_3(\text{H}_2\text{O})_3]\text{BiW}_9\text{O}_{33}]_2 \cdot 26\text{H}_2\text{O}$  polyoxometalate

The complex  $\text{Na}_{12}[\text{Cu}_3(\text{H}_2\text{O})_3]\text{BiW}_9\text{O}_{33}]_2 \cdot 26\text{H}_2\text{O}$  has a similar structure to the Krebs-type compounds, except that one group ( $\text{WO}_2$ ) is replaced by  $\text{Co}(\text{H}_2\text{O})_2$  (Figure 4.). Two cobalt atoms are similar, the third is different. The first cobalt atoms are bonded through two oxygen atoms from corner-sharing octahedra of one unit  $\beta\text{-B-}[\text{BiW}_9\text{O}_{33}]^{9-}$  and one oxygen atom from edge-sharing octahedra to the other unit  $\beta\text{-B-}[\text{BiW}_9\text{O}_{33}]^{9-}$ . The third cobalt atom is bonded through two oxygen atoms from two edge-sharing  $\text{WO}_6$  octahedra linked by common edges of each  $\alpha\text{-B-}[\text{BiW}_9\text{O}_{33}]^{9-}$  unit. Octahedral coordination geometry is satisfied by three water molecules water.

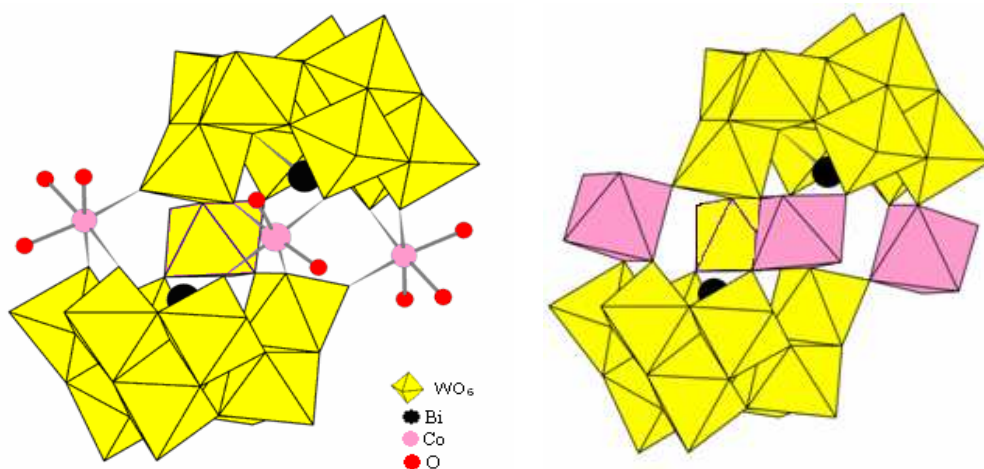


Figure 3. The structure of the  $\text{Na}_6\text{H}_4\{[\text{Co}(\text{H}_2\text{O})_3]_2\text{Co}(\text{H}_2\text{O})_2\}(\text{WO}_2)(\text{BiW}_9\text{O}_{33})_2 \cdot 27\text{H}_2\text{O}$  polyoxometalate

The chapter called **”Experimental details”** presents syntheses of polyoxometalates ligands and complexes and the methods used to characterize them. The most of the reaction mechanisms are very complex and they make the direct reaction pathway rather difficult. Experimental data shown that in this sort of synthesis three parameters are of extremely importance: concentration, pH and temperature.

The chapter called **„Special Applications of polyoxometalates”** relieve the catalytic properties of polyoxometalates complex and the influence of polyoxometalates on the on the growth of barley. The study of carbon paste electrode modified with undoped ZrO<sub>2</sub> and doped with H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> by cyclic voltammetry demonstrated their redox activity. Conductivity values obtained ( $10^{-4}$  -  $10^{-3}$  Ω<sup>-1</sup>cm<sup>-1</sup>) on the operating temperature range of fuel cell recommend use of ZrO<sub>2</sub> aerogels doped with H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> to yhe construction of solid electrolyte. The end of the thesis contains the study of the influence of polyoxometalates on the growth of barley plant. This study has attempted, within the limits possible, to bring more information in the field of biochemistry, researching the influence of polyoxometalates compounds on plants in general and in particular on barley culture. Even if their structures are more or less similar, all forms of polyoxometalates used in this experiment affect the germination and growth of barley plants.

**The present dissertation ends with conclusion, crystal data of four compounds and bibliography.**

## Conclusions

In this thesis were synthesized 21 compounds from which 17 have never been reported in the literature before.

Several investigation methods: elemental analysis, thermogravimetry, spectroscopic methods (FT-IR, Raman, UV, VIS, NMR), magnetic susceptibility measurements, cyclic voltammetry and X-ray diffraction cyclic voltammetry have been used in order to characterize the new compounds.

Elemental chemical analysis results are in good agreement with the compositions calculated from chemical formulas proposed.

Thermal behavior: compounds are dehydrated and decomposed in the wide range of temperatures, according to the class that they belong, losing in stages the crystallization and coordination water, the last one in parallel with decomposition of compounds.

IR spectra: were used to locate the bands characteristic to the polyoxometalates, and, above all, the identification of the position of the bands within  $1000-700\text{ cm}^{-1}$  that can be correlated with the lengths of the W-O bands and, where possible, with the results of the structural determinations. In the studied complexes, the tiny shift of the vibration frequencies corresponding to the  $\text{W}=\text{O}_t$  bonds can be noticed which correlates with the the lack of involvement of the terminal oxygen atoms in the coordination of the cations of transitional metals, excepting in the case of V(IV) complexes with an open Dawson-Wells structures where the terminal oxygen atoms are involved in coordination of vanadium ions. In the studied complexes, the strong shift of the vibration frequencies corresponding to the  $\text{W}-\text{O}_{c,e}-\text{W}$  bonds can be noticed, which correlates with the coordination of the transition cations through the oxygen atoms of the  $\text{O}_c$  and  $\text{O}_e$  type. The splitting of the bands corresponding to the  $\text{W}-\text{O}_{c,e}-\text{W}$  bonds in  $\text{Na}_{12}[\text{Cu}_3(\text{H}_2\text{O})_3]\text{BiW}_9\text{O}_{33}]_2 \cdot 26\text{H}_2\text{O}$   
 $\text{Na}_6\text{H}_4[\{(\text{Co}(\text{H}_2\text{O})_3)_2\text{Co}(\text{H}_2\text{O})_2\}(\text{WO}_2)(\text{BiW}_9\text{O}_{33})_2] \cdot 27\text{H}_2\text{O}$

$\text{Na}_6\text{H}_4[\{\text{Mn}(\text{H}_2\text{O})_3\}_2(\text{WO}_2)_2(\text{BiW}_9\text{O}_{33})_2] \cdot 41\text{H}_2\text{O}$  indicates the appearance of some very strong distortions in the trilacunary polyoxotungstenic fragments, as a result of the complexation.

The UV electronic spectra are characteristic to the polyoxometalates and similar to the ligand. The higher energy band ( $\nu_1$ ), due to the  $d_\pi\text{-p}_\pi$  proper transitions from the  $\text{W}=\text{O}_t$  bonds, insignificantly shifted in the complex polyoxotungstates compared to the ligands, which can be associated with the lack of involvement of the terminal oxygen atoms in the coordination of the cations of transitional metals. The lower energy band ( $\nu_2$ ), due to the  $d_\pi\text{-p}_\pi\text{-}d_\pi$  electronic transitions from the tricentric  $\text{W-O}_{c,e}\text{-W}$  bonds, displays, for both categories of polyoxowolframic complexes significant shifts towards lower energies compared to the ligands which is associated with the involvement of the oxygen atoms of these bonds in the coordination of the cations of the transitional metals.

Visible electronic spectra are characteristic to transition elements, were determined local symmetries coordinates of the transition ions. Visible electronic spectra indicated the octa-coordination of the  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{VO}^{2+}$  in octahedral environments (distorted  $\text{O}_h$  symmetry) in the complexes of the Krebs  $\text{K}_{10}[\text{M}^{2+}_2\text{Bi}_2\text{W}_{20}\text{O}_{70}(\text{H}_2\text{O})_6] \cdot 24\text{H}_2\text{O}$ .

$^{31}\text{P}$ -NMR spectra of polyoxometalates complex with phosphorus atom has a single broad signal due to paramagnetic cation of V (IV).

Cyclic voltammetry of the polyoxometalates complexes recorded in aqueous solutions showed two successive redox peak pairs in the negative potential range, which were attributed to two single electron tungsten centered processes. Electrochemical studies carried out indicate the movement of these peaks to more negative potential to trilacunary polyoxometalates, due to the coordinations of the transition cations. The waves from the positive potentials range are attributed to the redox processes in which the transitional metals are involved and they are the most active centers, being the first to obey to the redox processes.



Magnetic susceptibility measurements: the values of the magnetic moment and Curie-Weiss temperature indicates the existence of antiferromagnetic coupling and in complexes in which these measurements were made, we obtained an intermediate effective spin between 0 and the maximal possible value. Based on the magnetic susceptibility measurements it has been determined the effective magnetic moment of the compounds. These measurements together with the information obtained from EPR led to the establishment of intra- and intermolecular metal-metal interactions.

X-ray diffraction studies have demonstrated the molecular structure of complex  $\text{Na}_{12}[\text{Cu}_3(\text{H}_2\text{O})_3\text{BiW}_9\text{O}_{33}]_2 \cdot 26 \text{H}_2\text{O}$ ,  $\text{Na}_6\text{H}_4[\{\text{Mn}(\text{H}_2\text{O})_3\}_2(\text{WO}_2)_2(\text{BiW}_9\text{O}_{33})_2] \cdot 41\text{H}_2\text{O}$ ,  $\text{Na}_6\text{H}_4[\{\text{Co}(\text{H}_2\text{O})_3\}_2\text{Co}(\text{H}_2\text{O})_2\}(\text{WO}_2)(\text{BiW}_9\text{O}_{33})_2] \cdot 27\text{H}_2\text{O}$  and the possibility of self-assembling of the  $\text{K}_5[\text{PVW}_{11}\text{O}_{40}] \cdot 14 \text{H}_2\text{O}$  compound in supramolecular structures.

Synthesis of vanadil complexes of polyoxometalates from Keggin trilacunary precursor  $[\text{PW}_9\text{O}_{34}]^{9-}$ ,  $[\text{AsW}_9\text{O}_{34}]^{9-}$  in aqueous solution led by two different methods of synthesis to obtain two types of complexes polyoxometalates: Keggin polyoxometalates of V(IV) with monolacunary ligands and V(IV) complexes with an open Dawson-Wells structures. We can say that the anion  $[\text{X}_2\text{W}_{18}\text{O}_{66}]^{14-}$  where  $\text{X}=\text{P}^{5+}$ ,  $\text{As}^{5+}$ , is an intermediate species in the formation of Dawson-Wells tungstophosphate, respectively tungstoarsenate, which never knew until now.

Synthesis of cerium (III) complexes polyoxometalates was made from oxoanionic components to obtain sandwich complexes that seem more complicated as a normal sandwich due to the high coordination numbers of cerium which leads in this case to huge lobed structures.

Synthesis of  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{VO}^{2+}$  complexes polyoxometalates with Krebs structure was made from precursors:  $[\text{Bi}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$ ,  $[\text{Sb}_2\text{W}_{22}\text{O}_{74}(\text{OH})_2]^{12-}$ . For the first time in literature was elucidated the strengthening of the bonds of polyoxoanions to uranyl in the equatorial plane and the weakening of the bond  $\text{U}=\text{O}$  in the axial plane. Weakening of  $\text{U}=\text{O}$  axial bonds highlighted from Raman and UV-VIS spectra of the  $\text{Na}_{10}[(\text{UO}_2)_2(\text{H}_2\text{O})_2\text{Sb}_2\text{W}_{20}\text{O}_{70}] \cdot 28\text{H}_2\text{O}$ ,  $\text{Na}_{10}[(\text{UO}_2)_2(\text{H}_2\text{O})_2\text{Bi}_2\text{W}_{20}\text{O}_{70}] \cdot 34\text{H}_2\text{O}$

complex demonstrates the strengthening bond uranyl-polyoxometalate in the equatorial plane for U(VI) comparable to that of hydroxy-complex, holding the record for the Raman stretching frequency, of  $\text{UO}_2^{2+}$  lowest recorded to date.

Synthesis of  $\text{Cu}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Co}^{2+}$  complexes polyoxometalates was made from trilacunary pseudo-Keggin precursors  $[\text{BiW}_9\text{O}_{33}]^{9-}$  obtaining in the same reaction condition two types of polyoxometalates with different structures:  $[\text{Cu}_3^{2+}(\text{H}_2\text{O})_3(\text{BiW}_9\text{O}_{33})_2]^{12-}$  Hervè type,  $[\text{Mn}_2^{2+}(\text{H}_2\text{O})_6(\text{BiW}_9\text{O}_{33})_2(\text{WO}_2)_2]^{10-}$  and  $[\text{Co}_3^{2+}(\text{H}_2\text{O})_8(\text{BiW}_9\text{O}_{33})_2(\text{WO}_2)]^{10-}$  Krebs type which justifies the balance between oxoanions precursors and polyoxotungstate fragments existing in aqueous solutions at different pH.

The most important field of application for polyoxometalates is homogeneous and heterogeneous catalysis. Approximately 80-85% of the patents from literature investigate polyoxometalates in terms of their catalytic applications

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